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# **Orientational Pair Correlation, Polar Order Parameter and Temporal Stability in the Second Harmonic Generation of Amorphous Polymers**

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### Abstract

Measurements of the second harmonic generation (SHG) signal were made on the DAN/PMMA guest/host system as a function of the nonlinear optical (NLO) chromophore concentration and the poling field strength. The temporal stability of the SHG signal, after the poling field was removed, was also investigated. The polar orientational order parameters,  $L_{33}$  and  $L_{31}$  (see text for definition), were deduced from the second order nonlinear susceptibility. Both of the polar orientational order parameters and the relaxation time of the nonlinear susceptibility were found to increase with increasing NLO chromophore concentration. The concentration dependence was interpreted as due to the anisotropic intermolecular interaction, particularly the dipole-dipole interaction. The anisotropic intermolecular interaction introduces the orientational pair correlation function which enhances the polar order as well as the temporal stability of the NLO effect.

## I. Introduction

The second order nonlinear optical effect in the amorphous polymer lies in the existence of the polar orientation order induced by the externally applied electric field. The external electric field aligns molecular chromophores which possess a large hyperpolarizability. This type of polymeric material, while combining the processability and excellent transparency characteristics of an amorphous glassy polymer, represents a new class of optical materials that show a great promise for the development of electro-optical devices and second harmonic generation applications.<sup>1,2</sup>

To maximize the nonlinear optical (NLO) effect it is important to understand the behavior of the polar order parameter (POP) in association with the effect of the electric field poling process. Several methods have been employed to develop materials with large second order optical susceptibilities and enhanced stability. The incorporation of the NLO chromophore molecules, by covalently bonding them to polymer chains, greatly restricts the reorientational mobility of the chromophores and significantly improves the NLO stability. The covalent bonding of the NLO chromophores to polymers can be incorporated at the side chain,<sup>3</sup> main chain<sup>4</sup> or through crosslinkage.<sup>5</sup> For the chromophore-doped polymer guest/host system, relaxation is rapid and second harmonic generation efficiency is generally short-lived.<sup>6</sup> However, due to its ease of sample preparation with well controlled chromophore concentration, the chromophore doped material provides a well defined system to delineate various physical mechanisms that affect the alignment and stability of the NLO chromophore/polymer system.

In this paper we are concerned with the concentration dependence of the POP and the relaxation of the POP. The concentration dependence of the POP and the relaxation time of the POP is interpreted as being due to the pair orientational correlation arising from the anisotropic intermolecular interaction of the NLO chromophores.

## II. Experimental

Appropriate amounts of 4-(N,N'-dimethylamino-3-acetamidonitrobenzene) DAN and (Poly (methyl) Methacrylate) PMMA were dissolved in chloroform to form solutions of different chromophore concentrations. The volume of chloroform in each solution was adjusted to give a desired viscosity suitable for spin coating. The solutions were filtered to remove undissolved particulates. Films were prepared by spin coating the polymer solution on soda lime glass slides, which were precoated with 300 Å SiO<sub>2</sub> and 250 Å ITO (indium tin oxide) films. The NLO polymer/ITO sample assembly was placed in a vacuum oven first at 40°C for over 24 hours and then baked at the temperature slightly above the glass transition temperature. The absence of solvent was checked with infrared spectrometry after the baking process, no solvent IR absorption band can be detected. After certifying the chromophore concentration, another ITO glass slide was then placed on top of the polymer/ITO glass slide to form a sandwich configuration for electrode poling. The glass transition temperature ( $T_g$ ) of the sample was determined by using a DSC (Differential Scanning Calorimeter, Perkin Elmer Delta series). The refractive index, and the thickness of the sample, were determined by a prism coupler (Matricon) modified for the multiple wavelength operation.

The second harmonic generation (SHG) was carried out using an apparatus similar to that reported by Guan and Wang<sup>7</sup>. It consists of an Nd:YAG laser (Spectra-Physics GCR-11,  $\lambda = 1.06 \mu\text{m}$ , Q switched at 10 Hz), a computer controlled goniometer stage, a series of short-pass and long-pass filters, a polarizer, a half wave plate, a photomultiplier tube, and a boxcar integrator which was interfaced to a PC. The sample assembly mounted on the goniometer stage was placed in an oven which is temperature controlled to the accuracy of  $\pm 0.5^\circ\text{C}$ . The electric field poling was carried out inside the temperature controlled oven. To obtain the signal decay measurement the electric field was switched off and the electrodes were grounded, after the

sample signal had reached a stabilized steady state in a constant temperature environment.

The Maker fringe of a Y-cut single crystal quartz plate ( $d_{11} = 0.5$  pm/V) was used as the reference to determine the second order susceptibility of the sample.

### III. Results and Discussion

Shown in Fig. 1 are the temporal characteristics of the boxcar SHG output signals for a DAN/PMMA film (DAN is 10 wt%) at 84°C, poled with various levels of the electric field amplitude. The sample assembly that was used to obtain signals given in Fig. 1 was oriented with the angle of incidence  $\phi = 50^\circ$ . The incident laser beam was at the p-polarization. At this orientation the SHG signal was at its maximum value with respect to the SHG signal versus  $\phi$  plot.

Several observations can be made in Fig. 1: 1) The SHG signal increases steadily with increasing poling field strength; 2) The leading edge of the SHG signal is sharp; 3) considerable signal fluctuations are noted at the maximum amplitude; 4) After the poling field is switched-off the signal falls off rapidly, and then is followed by a slower decay. We have investigated these features and now describe the result in more detail.

The SHG signal ( $I_{\text{SHG}}$ ) has been investigated as a function of the poling field strength at various NLO chromophore concentrations. Shown in Fig. 2 is the plot of the SHG signal (for 10 wt% DNA in PMMA at 84°C) as a function of  $E_p^2$ , the square of the strength of the electric field. To determine the value of  $E_p$ , we used the film thickness data, determined from the waveguiding experiment using the Matricon, which simultaneously provides the refractive index and the film thickness data (film thickness is  $3.89 \mu\text{m}$  for the 10 wt% film). In the  $0.6$  to  $1.3 \times 10^6$  volt/cm range,  $I_{\text{SHG}}$  appears to vary linearly with the poling field as  $E_p^2$ .

For an isotropic film subject to a poling field in the direction perpendicular to the film surface, the transmitted second harmonic intensity  $I_{2\omega}$  ( $= I_{\text{SHG}}$ ) excited with the incident

fundamental beam in the p-polarization is given by

$$I_{2\omega} = \frac{(8\pi)^3}{c} t_0^2 I_\omega^2 \chi_{\text{eff}}^{(2)}(\phi) \frac{T_{2\omega}(\phi)}{(n_\omega^2 - n_{2\omega}^2)} \sin^2 \left( \frac{\pi \ell}{2\ell_c} \right) \quad (1)$$

where  $c$  is the velocity of light in vacuum;  $t_0$  is the transmission coefficient of the second harmonic light through the substrate.  $I_\omega$  is the intensity of the fundamental beam inside the medium.  $T_{2\omega}(\phi)$  is the transmission factor, which depends on the polarization of the incident beam,  $\phi$  the angle of incidence, as well as the refractive index of the material at the fundamental ( $n_\omega$ ) and doubled ( $n_{2\omega}$ ) frequencies. We have modified the calculation of  $T_{2\omega}(\phi)$  given by Jerphagnon and Kurtz<sup>8</sup> for the sample geometry appropriate for the contact electrode poling and corona poling techniques.<sup>7</sup> The  $T_{2\omega}(\phi)$  expression appropriate for the present experiment is

$$T_{2\omega}(\phi) = \frac{2n_{2\omega} \cos \phi_{2\omega}' (n_\omega \cos \phi + n_0 \cos \phi_\omega') (n_{2\omega} \cos \phi_\omega' + n_\omega \cos \phi_{2\omega}')}{(n_{2\omega} \cos \phi + n_0 \cos \phi_{2\omega}')^2 (n_{2\omega} \cos \phi + n_0 \cos \phi_{2\omega}')} \quad (2)$$

where  $n_0$  is the refractive index of the front and back substrates;  $\phi_\omega'$  and  $\phi_{2\omega}'$  are the angles of refraction of the fundamental and the second harmonic beams inside the medium, respectively. They are related to the incident angle  $\phi$  by Snell's law:  $\sin \phi_\omega' = n_0 \sin \phi / n_\omega$  and  $\sin \phi_{2\omega}' = n_0 \sin \phi / n_{2\omega}$ . The quantity  $\ell_c$  is the correlation length given by  $\ell_c = \lambda/4 |n_\omega \cos \phi_\omega' - n_{2\omega} \cos \phi_{2\omega}'|$ . Finally, the effective optical susceptibility ( $\chi_{\text{eff}}$ ) for the optical field in the plane of incidence (in the p-polarization) is given by

$$\chi_{\text{eff}}^{(2)} = [\chi_{31}^{(2)} \sin \phi_\omega' \cos \phi_\omega' \cos \theta_{2\omega}' + (\chi_{33}^{(2)} \sin^2 \phi_\omega' + \chi_{31}^{(2)} \cos^2 \phi_\omega') \sin \phi_{2\omega}'] \quad (3)$$

In Eqs. (2) and (3), we follow ref. 8 by designating the quantity inside the NLO medium by a prime.

The two SHG susceptibility elements  $\chi_{31}^{(2)}$  and  $\chi_{33}^{(2)}$  are related to the  $\theta$  polar orientational order parameter  $L_{31} = \frac{1}{2} (\langle \cos \theta_1 \rangle - \langle \cos^3 \theta_1 \rangle)$  and  $L_{33} = \langle \cos^3 \theta_1 \rangle$  by<sup>9</sup>

$$\chi_{31}^{(2)} = \rho \beta f_{2\omega} f_{\omega}^2 L_{31} \quad (4)$$

and

$$\chi_{33}^{(2)} = \rho \beta f_{2\omega} f_{\omega}^2 L_{33} \quad (5)$$

where  $\rho$  is the number density of the chromophores and  $\beta$  is dominant component of the second order hyperpolarizability tensor along the molecular axis. In the Lorentz model the local field factors  $f_{2\omega}$  and  $f_{\omega}$  are given by  $f_{2\omega} = (n_{2\omega}^2 + 2)/3$  and  $f_{\omega} = (n_{\omega}^2 + 2)/3$ .

In the POP expressions the subscript 1, associated with  $\theta$ , refers to the representative NLO chromophore 1.

For a system of non-interacting NLO chromophores, the two POP's are given by

$$L_{33} = \mathcal{L}_3(a) = \left(\frac{6}{a^3} + 1\right) \coth a - \left(\frac{6}{a^3} + \frac{3}{a}\right) \quad (6)$$

and

$$L_{31} = \frac{1}{2} [\mathcal{L}_1(a) - \mathcal{L}_3(a)] = \left(\frac{3}{a^3} + \frac{1}{a}\right) - \frac{3}{a^3} \coth a \quad (7)$$

where  $\mathcal{L}_1$  and  $\mathcal{L}_3$  are the Langevin function of order 1 and 3, respectively. The quantity  $a$  is equal to  $f_0 \mu E_p / kT$ ,  $f_0$  is the local field factor introduced to account for the presence of the polymer host,  $\mu$  is the ground state dipole moment.

In the independent dipole reorientation model, the orientation of the dipoles is completely dictated by the external field, and the polar order parameters  $L_{31}$  and  $L_{33}$  are practically independent of the concentration of the NLO chromophores, due to the fact that in this approximation the potential energy of the interaction of the NLO molecules does not play a role in affecting the values of POP.

In the case of the poling parameter  $a \ll 1$ ,  $L_{31}$  and  $L_{33}$  reduce to:



$$L_{33} = \frac{a}{5} + \dots \quad (8)$$

$$L_{31} = \frac{a}{15} + \dots \quad (9)$$

Thus, under this simplified case the NLO susceptibility  $\chi_{33}^{(2)}$  (or  $\chi_{31}^{(2)}$ ) is proportional to the poling field  $E_p$ ; hence, the SHG intensity is proportional to  $E_p^2$ , consistent with the result shown in Fig. 2. The ratio of  $\chi_{33}^{(2)}/\chi_{31}^{(2)}$  is equal to 3.

We have determined the NLO susceptibilities  $\chi_{31}^{(2)}$  and  $\chi_{33}^{(2)}$  by fitting to Eq. (1) the measured intensities versus  $\phi$  data, with the incident fundamental beam in the p polarization, assuming  $\chi_{33}^{(2)}/\chi_{31}^{(2)} = 3$ .

An independent check of the fitting procedure was also carried out without making the  $\chi_{33}^{(2)}/\chi_{31}^{(2)} = 3$  assumption, but using the measured SHG intensities obtained by the fundamental beam in both the s and p polarizations, a method similar to that described in ref. 7. Within experimental uncertainty the susceptibility results are in agreement with that obtained by the  $\chi_{33}^{(2)}/\chi_{31}^{(2)} = 3$  assumption.

Having obtained the  $\chi_{33}^{(2)}$  and  $\chi_{31}^{(2)}$  values, we can calculate the POP  $L_{33}$  and  $L_{31}$ , using Eqs. (4) and (5). We have found that both  $L_{33}$  and  $L_{31}$  depend on the NLO chromophore concentration. This result is consistent with that found in the MNA/PMMA (MNA, 2-methyl 4 nitroaniline)<sup>7</sup>, but is not in agreement with that predicted by the independent dipole orientation model described above.

In Fig. 3, we have plotted  $L_{33}$  as a function of the DAN concentration (in number density). The  $\beta$ -value that was needed for calculating  $L_{33}$  (c.f. Eq. (4)) was obtained from the paper by Eaton<sup>10</sup>. One notes that over the concentration range of  $1 \times 10^{20}$  to  $3.7 \times 10^{20}$  chromophores/cm<sup>3</sup>,  $L_{33}$  increases from 0.28 to 0.38.

As recently shown by Wang,<sup>11</sup> the concentration dependence of POP is due to the

orientational pair correlation that arises from the angular dependence, or anisotropic intermolecular potential between NLO chromophores. In ref. 11, it is shown that while any type of anisotropic intermolecular potential (whether it be short or long range interaction) can affect the POP induced by the external electric field. The dipole-dipole interaction makes the most important contribution because of its long range interaction.

In the case of the weak field poling condition ( $a \ll 1$ ) Wang shows that <sup>11</sup>

$$L_{33} = a (1 + \rho G_{\Delta})/5 \quad (10)$$

and

$$L_{31} = a (1 + \rho G_{\Delta})/15 \quad (11)$$

where  $G_{\Delta}$  is the cluster integral associated with the solution of the molecular pair correlation function. In the case of the dipole-dipole interaction, the cluster integral can be related to the Kirkwood g-factor,  $g_K$ , that arises from the dielectric theory of the polar fluid by<sup>12</sup>

$$\rho G_{\Delta} = g_K - 1 \quad (12)$$

Since  $g_K$  increases with increasing  $\rho$  and is in general greater than one, one expects that  $L_{33}$  (or  $L_{31}$ ) increases with increasing the NLO chromophore density, consistent with the result of Fig. 3. In ref. 7, it is further shown how the dielectric constant of the combined chromophore/polymer medium affects the NLO susceptibility, due to the orientational pair correlation.

The orientational pair correlation not only affects the NLO susceptibility, it also affects the relaxation behavior of the NLO susceptibility. The relaxation behavior is directly associated with the temporal stability of the nonlinear optical effect. Shown in Fig. 4 are the representative temporal characteristics for a DAN (10 wt %) doped PMMA film at 68°C. In this work the sample is first equilibrated at a chosen temperature (68°C for that of Fig. 4) then the poling field is applied. After the SHG signal reaches a stable maximum value, the poling field is then

switched off and the electrodes are shorted.

As one notes, the SHG signal decay behavior cannot be fit to a single exponential. The signal first assumes an initial rapid decay and is then followed by a long decay to the background. As shown previously, either for the guest/host<sup>6,13</sup> or for the chromophore functionalized NLO polymer,<sup>4</sup> the SHG signal can be satisfactorily described by a fit of nonlinear optical susceptibility to a biexponential form as

$$d_{33} = \frac{1}{2} \chi_{33}^{(2)} = ae^{-t/\tau_1} + be^{-t/\tau_2} \quad (13)$$

where  $a + b$  is equal to the initial value of the nonlinear optical coefficient.

Torkelson *et al.*<sup>14</sup> speculated that the biexponential decay is due to the free volume distribution in the glassy polymer, consisting of liquid-like and solid-like regions. The initial rapid decay is associated with the free volume distribution in the liquid-like region in which reorientation of the chromophore dipole moment is rapid, even though the polymer is in the glassy state. In the guest/host system we found that the initial amplitude decrease depends on the strength of the poling field. This suggests that the initial decrease is probably associated with the third order effect similar to that seen in EFISH (electric field induced second harmonic generation). The time constant,  $\tau_1$ , characterizing the initial decay represents an effective relaxation time, which also convolutes the time of switching off the poling field. However, due to the slow switching-off electronics used in the present experiment, the time constant  $\tau_1$  does not reflect the true third order effect suggested above. Fast electronics, as well as mode-locked laser pulses in the pico or subpico-second duration, are needed to clarify the nature of the fast initial decay.

Nevertheless, the second slow decay, does not depend on the poling field, but strongly depends on temperature as well as the chromophore concentration. The slow decay, with the time

constant characterized by  $\tau_2$ , is associated with the orientational relaxation of the chromophores in the polymer matrix. As the temperature increases the relaxation decreases the polar order and hence the SHG signal stability. We shall report the temperature dependence of  $\tau_2$  elsewhere and consider here only its concentration dependence.

The relaxation time  $\tau_2$  extracted from fitting the nonlinear optical susceptibility  $d_{33}$  in accordance with Eq. (13) is plotted in Fig. 5 as a function of NLO chromophore concentration. The data points represent values obtained for the film at 68°C and poled at field of  $.89 \times 10^6$  volt/cm. Interestingly, one notes that  $\tau_2$  increases with increasing NLO chromophore concentration, suggesting that the increase in the loading of the NLO chromophore density slows down the SHG signal relaxation and enhances the stability.

In general, doping the polymer with small molecules plasticizes the polymer and lowers its glass transition temperature  $T_g$ . For example, doping 5 wt % of DAN in amorphous PMMA depresses the  $T_g$  from 107 to 87°C. Lowering the  $T_g$  increases the mobility of the NLO chromophore, and thus we expect  $\tau_2$  to decrease with increasing chromophore concentration. This is contrary to the result shown in Fig. 5, which indicates that  $\tau_2$  steadily increases with increasing chromophore concentration. The increase in  $\tau_2$  with increasing  $\rho$  is due to the orientational pair correlation factor. It can be shown that if  $\tau_s$  represents the reorientational relaxation time of an uncorrelated NLO chromophore, then  $\tau_2$  is related to  $\tau_s$  by<sup>15</sup>

$$\tau_2 = \tau_s (1 + \rho G_\Delta) / (1 + \rho F) \quad (14)$$

where  $\rho G_\Delta$  represents the orientational pair correlation factor introduced previously, and  $\rho F$  represents the dynamic orientational pair correlation (DOPC) factor. This situation is quite similar to light scattering in which the reciprocal of the linewidth of the depolarized Rayleigh spectrum of a system of optically anisotropic molecules is proportional to the orientational relaxation time  $\tau_R$ .<sup>16</sup> The orientational relaxation time  $\tau_R$  is affected by the static and dynamic

orientational pair correlation in a manner described by Eq. (14). In the present situation, we are concerned with the orientational relaxation associated with the polar order  $L_{33}$ , rather than the relaxation of quadrupolar order involved in light scattering.

However, it appears that the concentration dependence of  $\tau_2$  involved in SHG is considerably more pronounced than that observed in light scattering. Comparing the concentration dependence of  $\tau_2$  with that of  $L_{33}$ , one notes that over the same concentration range,  $\tau_2$  increases by a factor of more than 4 (from 240 sec. at  $\rho = 1 \times 10^{20}/\text{cm}^3$  to 1025 sec. at  $\rho = 3.7 \times 10^{20} (\text{cm}^3)$ ) in contrast to a factor of about 1.4. The larger increase in  $\tau_2$  indicates that the (DOPC) factor, as given in Eq. (14), is probably negative, which decreases the denominator as  $\rho$  increases, despite the factor that in light scattering the DOPC factor is known to be small and often negligible. Clearly, in order to improve our understanding of the effect of orientational pair correlation on the relaxation behavior of the SHG signal, additional work is needed.

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### Figure Captions

**Fig. 1** The boxcar SHG signal output signals for a DNA/PMMA film at 84°C, poled with various levels of the electric field strength. 1:  $.61 \times 10^6$  volt/cm; 2:  $.77 \times 10^6$  volt/cm; 3:  $.89 \times 10^6$  volt/cm; 4:  $1.04 \times 10^6$  volt/cm; 5:  $1.19 \times 10^6$  volt/cm; 6:  $1.31 \times 10^6$  volt/cm

**Fig. 2** The SHG signal (arbitrary unit) of a DNA/PMMA film (DAN 10 wt %) plotted versus  $E_p^2$ . The linearity indicates that the sample is poled under the weak poling condition.

**Fig. 3** The polar orientational order parameter  $L_{33}$  plotted versus number density ( $\rho$ ) of DAN in the DAN/PMMA film.

**Fig. 4** The temporal characteristic of the SHG signal from a 15 wt% DAN/PMMA film poled with an electric field at  $.89 \times 10^6$  volt/cm.

**Fig. 5** The relaxation time  $\tau_2$  plotted versus number density  $\rho$  of DAN in the DAN/PMMA film.











